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(54) PIEZOELECTRIC CERAMIC COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a piezoelectric ceramic composition having good piezoelectric characteristics and a sufficient mechanical strength in combination.

SOLUTION: This piezoelectric ceramic composition obtained by adding at least one kind of metal or metal oxide selected from the group consisting of Pd, B₂O₃, MgO, Al₂O₃, SiO₂, Sc₂O₃, V₂O₅, Cr₂O₃, Mn₃O₄, Fe₂O₃, CoO, NiO, CuO, ZnO, GeO₂, Y₂O₃, Nb₂O₅, MoO₃, SnO₂, Sb₂O₃, HfO₂, Ta₂O₅, WO₃, Bi₂O₃, CeO₂, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, TbO, Dy₂O₃, Ho₂O₃, Er₂O₃, Yb₂O₃ and LuO to an oxide composition represented by the basic compositional formula [Pba1Aa2][B1B2]xTiyZrz]O3 (wherein A is at least one kind of element selected from Ca, Sr, Ba and La; B1 is Sn, Zn, Cd, Mg, Ni, Co, Fe, Sc, Yb, Lu, In or Mn; and B2 is Sb, Nb, Ta, W or Te).

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(54) 【発明の名称】 圧電セラミック組成物

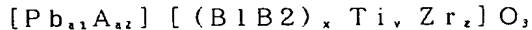
(57) 【要約】

【課題】 良好な圧電特性と十分な機械的強度を併せ持つ圧電セラミック組成物を提供する。

【解決手段】 基本組成式 $[Pb_{1-x}A_x] [(B1B2)_xTi_yZr_z]O_3$ (式中、AはCa、Sr、BaおよびLaから選ばれる少なくとも一種の元素であり；B1はSn、Zn、Cd、Mg、Ni、Co、Fe、Sc、Yb、Lu、InまたはMnであり；B2はSb、Nb、Ta、WまたはTeである) で表される酸化物組成物に対して、Pd、 B_2O_3 、MgO、 Al_2O_3 、 SiO_2 、 Sc_2O_3 、 V_2O_5 、 Cr_2O_3 、 Mn_2O_3 、 Fe_2O_3 、CoO、NiO、CuO、ZnO、 GeO_2 、 Y_2O_3 、 Nb_2O_5 、 MoO_3 、 SnO_2 、 Sb_2O_3 、HfO₂、 Ta_2O_5 、 WO_3 、 Bi_2O_3 、 La_2O_3 、 CeO_2 、 Pr_6O_{11} 、 Nd_2O_3 、 Sm_2O_3 、 Eu_2O_3 、Gd₂O₃、TbO₃、 Dy_2O_3 、 Ho_2O_3 、 Er_2O_3 、 Yb_2O_3 、およびLuOからなる群より選ばれる少なくとも一種の金属または酸化物を添加する。

【特許請求の範囲】

【請求項1】 基本組成式：



（式中、AはCa、Sr、BaおよびLaから選ばれる少なくとも一種の元素であり；B1はSn、Zn、Cd、Mg、Ni、Co、Fe、Sc、Yb、Lu、InまたはMnであり；B2はSb、Nb、Ta、WまたはTeであり；またa1、a2、x、yおよびzはそれぞれ、条件式：

$$x+y+z=1$$

$$0.05 \leq x \leq 0.40$$

$$0.1 \leq y \leq 0.5$$

$$0.2 \leq z \leq 0.6$$

$$0.97 < (a1+a2) < 1$$

を満たす原子比であり、ただしa1は0ではないが、a2は0であることができる）で表される酸化物組成物に対して、Pd、B₂O₃、MgO、Al₂O₃、SiO₂、Sc₂O₃、V₂O₅、Cr₂O₃、Mn₂O₃、Fe₂O₃、CoO、NiO、CuO、ZnO、GeO₂、Y₂O₃、Nb₂O₅、MoO₃、SnO₂、Sb₂O₃、HfO₂、Ta₂O₅、WO₃、Bi₂O₃、La₂O₃、CeO₂、Pr₆O₁₁、Nd₂O₃、Sm₂O₃、Eu₂O₃、Gd₂O₃、Tb₂O₃、Dy₂O₃、Ho₂O₃、Er₂O₃、Yb₂O₃、およびLu₂O₃からなる群より選ばれる少なくとも一種の金属または酸化物を0.01重量%～1重量%添加してなることを特徴とする圧電セラミック組成物。

【請求項2】 前記酸化物に代えて、焼成により前記酸化物に成り得る物質を添加してなる請求項1記載の圧電セラミック組成物。

【請求項3】 結晶粒径が0.1μm以上で5μm以下である請求項1または2記載の圧電セラミック組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、圧電セラミック組成物、特に基本組成式 $[\text{Pb}_{1-x}\text{A}_x][(\text{B}_1\text{B}_2)_x\text{Ti}_y\text{Zr}_z]\text{O}_3$ で表される酸化物組成物に、添加物として特定の金属または酸化物を添加してなる圧電セラミック組成物に関する。

【0002】

【従来の技術】従来、三元系圧電セラミック組成物の改良に関するものとして $[\text{Pb}_b\text{Sr}_b\text{Ba}_c]_a \cdot [(\text{Zn}_{1-x}\text{Nb}_x)_2\text{Ti}_x\text{Zr}_y]_b\text{O}_3$ からなる圧電セラミック組成物があり（特開平3-256379号）、A/Bの値を特定の範囲に設定することで、音響変換器としての使用に適した大きな圧電定数を持たせた圧電セラミック組成物が開示されている。また、 $(\text{Pb}_{1-x}\text{M}_x)(\text{Mg}_{1-y}\text{Nb}_y)_2\text{Ti}_x\text{Zr}_y\text{O}_3$ で表される酸化物組成物において、 $b=0.005\sim0.05$ とすることで、電気機械結合係数および誘電率を高くできることが知られている（特公平4-78582号）。

【0003】

【発明が解決しようとする課題】圧電セラミック材料

は、圧電フィルター、圧電トランス、超音波振動子、圧電アクチュエータ、圧電ブザー等、種々の用途に広範囲に使用されている。中でも、近年、圧電発音体、圧電アクチュエータ等の圧電振動子は小型化、薄層化が進んでいる。特に、圧電アクチュエータ等の電子部品の分野においては、例えばパソコン用のハードディスクドライブヘッド等のためのマイクロアクチュエータとして、記録密度の向上に伴い、サブミクロンオーダーの微小変位を提供できる超小型の圧電アクチュエータの開発が盛んに行われている。

【0004】圧電材料を、例えば変位制御用アクチュエータとして使用する場合、その変位性能を高めるためには圧電定数(d)を大きくする必要がある。一般に、圧電材料においては、圧電定数(d)と、電気機械結合係数(k)及び比誘電率(ε)との間に $d \propto k \sqrt{\epsilon}$ なる関係があり、圧電定数(d)を大きくするためには、電気機械結合係数(k)および比誘電率(ε)を大きくしなければならない。かかる観点から、従来、優れた圧電特性を有する圧電セラミック組成物が種々開発されてきた。

【0005】しかし、従来の組成の圧電セラミック材料は、優れた圧電特性を有するものの、機械的強度が必ずしも十分でないという問題点を有していた。すなわち、これら材料を上記アクチュエータ等に使用した場合、素子に加工する際に割れや欠け等の不良が生じたり、その構造材料に近い性格のために外からの応力により割れが生じたりするという欠点があった。また、素子の駆動に際して、大きな変位量を得るために大きな電圧を印加した場合、その機械的強度が不十分なためにその変位自体によって破壊に至る場合があるという欠点もあった。

【0006】従って、本発明は、優れた比誘電率、電気機械結合係数、圧電特性を有しながら、超小型、薄型の素子に加工した場合にも十分な機械的強度を有する圧電セラミック組成物を提供することを目的とするものである。

【0007】

【課題を解決するための手段】本発明に係る組成物は、基本組成式 $[\text{Pb}_{1-x}\text{A}_x][(\text{B}_1\text{B}_2)_x\text{Ti}_y\text{Zr}_z]\text{O}_3$ で表される酸化物組成物においてa1+a2の値、すなわち[PbA]サイトの組成比の[(B1B2)TiZr]サイトの組成比に対する比（以下A/Bという）を1より小さくし、且つ添加物として特定の金属または酸化物を特定の量添加したときに、良好な比誘電率、電気機械結合係数、圧電特性を維持しながら、機械的強度、特に抗折強度が向上するという発見に基づいている。

【0008】かかる発見に基づく本発明は、基本組成式：

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$[Pb_{a1}A_{a2}][(B1B2)_xTi_zZr_z]O_3$
 (式中、AはCa、Sr、BaおよびLaから選ばれる少なくとも一種の元素であり；B1はSn、Zn、Cd、Mg、Ni、Co、Fe、Sc、Yb、Lu、InまたはMnであり；B2はSb、Nb、Ta、WまたはTeであり；またa1、a2、x、yおよびzはそれぞれ、条件式：

$$x+y+z=1$$

$$0.05 \leq x \leq 0.40$$

$$0.1 \leq y \leq 0.5$$

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を満たす原子比であり、ただしa1は0ではないが、a2は0であることができる)で表される酸化物組成物に対して、Pd、B₂O₃、MgO、Al₂O₃、SiO₂、Sc₂O₃、V₂O₅、Cr₂O₃、Mn₂O₄、Fe₂O₃、CoO、NiO、CuO、ZnO、GeO₂、Y₂O₃、Nb₂O₅、MoO₃、SnO₂、Sb₂O₃、HfO₂、Ta₂O₅、WO₃、Bi₂O₃、La₂O₃、CeO₂、Pr₆O₁₁、Nd₂O₃、Sm₂O₃、Eu₂O₃、Gd₂O₃、Tb₂O₃、Dy₂O₃、Ho₂O₃、Er₂O₃、Yb₂O₃、およびLuOからなる群より選ばれる少なくとも一種の金属または酸化物を0.01重量%～1重量%添加してなることを特徴とする圧電セラミック組成物である。本発明においては、上記のようにa1+a2すなわちA/Bの値が0.97より大きく、かつ1より小さいことが望ましい。A/Bの値が0.97以下になると、必要な高い比誘電率、電気機械結合係数ひいては圧電特性が得られなくなり易い。また、A/Bの値が1以上になると、必要な高い機械的強度、例えば後述する測定法で測定したときに100MPa以上の機械的強度を得られなくなる場合がある。

【0009】

【発明の実施の形態】次に、本発明の圧電セラミック組成物の好ましい実施形態を説明する。まず、出発材料として、酸化物、または炭酸塩、硝酸塩もしくは水酸化物のような焼成により酸化物に代わり得る化合物を用い、それらを所定の最終組成を与える量比となるように秤量し、ボールミル等を用いて湿式混合する。この湿式混合の際のスラリー媒体としては、水またはエタノール等のアルコール、あるいは水とアルコールとの混合物を用いることが好ましい。

【0010】本発明においては、好ましくはこの混合時、あるいは後述する仮焼き後に、前記出発原料に対して、Pd、B₂O₃、MgO、Al₂O₃、SiO₂、Sc₂O₃、V₂O₅、Cr₂O₃、Mn₂O₄、Fe₂O₃、CoO、NiO、CuO、ZnO、GeO₂、Y₂O₃、Nb₂O₅、MoO₃、SnO₂、Sb₂O₃、HfO₂、Ta₂O₅、WO₃、Bi₂O₃、La₂O₃、CeO₂、Pr₆O₁₁、Nd₂O₃、Sm₂O₃、Eu₂O₃、Gd₂O₃、Tb

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O、Dy₂O₃、Ho₂O₃、Er₂O₃、Yb₂O₃、およびLuOからなる群より選ばれる少なくとも一種の金属または酸化物を、出発原料の合計重量を基準として0.01重量%～1重量%の量添加する。かかる酸化物の複数を組み合わせて用いる場合には、複数の合計の添加量が0.01重量%～1重量%であることが好ましい。なお、添加量が0.01重量%に満たない場合は、添加物の効果が認められず、一方、添加量が1重量%を超えると、却って誘電率、電気機械結合係数の低下等の悪影響が顕著になる。

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【0011】尚、本発明においては、上記酸化物に代えて、焼成により上記酸化物に成り得る物質、例えば炭酸塩、硝酸塩、水酸化物あるいは金属等を添加してもよい。上記酸化物に代えて、かかる物質を添加する場合、その添加量は、対応する酸化物の重量に換算して0.01重量%～1重量%（出発原料の合計重量基準）とすることが好ましい。かかる物質の複数を組み合わせて用いる場合には、上記と同様に、それぞれの対応する酸化物の重量に換算したときの合計量が0.01重量%～1重量%であることが好ましい。

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【0012】出発原料を十分に混合した後、約800～約1000℃の温度において約1～約3時間仮焼きし、得られた仮焼き物をスラリー化し、ボールミル等を用いて湿式粉碎する。この湿式粉碎の際のスラリー媒体としては、水またはエタノール等のアルコール、あるいは水とアルコールとの混合物を用いることが好ましい。なお、この湿式粉碎は、仮焼き物の粉碎粒子の平均粒径が0.5～2.0μm程度になるまで行うことが好ましい。

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【0013】湿式粉碎後、得られた仮焼き物の粉末を乾燥し、乾燥物に水または、例えばポリビニルアルコール等のバインダーを少量（0.5重量%～8重量%）添加し、98～392MPa（1～4tf/cm²）の圧力でプレス成形して、成形体を得る。なお、成形法としては、押し出し成型法や、本技術分野で通常使用される他の成型法を使用することもできる。

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【0014】次いで成形体を焼成し、圧電セラミックスを得る。焼成温度は、好ましくは1060℃～1200℃の範囲内の温度を選択する。また、焼成時間は、好ましくは1～4時間程度とする。焼成は大気中で行ってもよく、また大気中よりも酸素分圧の高い雰囲気や、純酸素雰囲気中に行ってもよい。

【0015】本発明においては、焼成の際、得られるセラミックスの結晶粒径が0.1μm以上、5μm以下となるようにすることが好ましく、5μmより大きく粒成長させると機械的強度が低下する傾向が見られる。

【0016】

【実施例】

【実施例1】出発原料としてPbO、TiO₂、ZrO₂、CoO、Nb₂O₅、SrCO₃、添加物としてWO

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を用い、それらを所定の最終組成を与える量比となるよう秤量し、配合した後、ボールミルを用いて5時間湿式混合した。湿式混合の際、スラリー媒体としては水を使用した。次いで混合物を900℃において2時間仮焼成し、その後ボールミルを用いて15時間湿式粉碎した。湿式粉碎の際、スラリー媒体としては水を使用した。スラリーを乾燥後、粉末状の乾燥物に水を6重量%添加し、39.2MPa(400kgf/cm²)の圧力下で一軸加圧成形して円柱を作製し、これに392MPa(4t/cm²)の冷間静水圧成形を行った。この円柱を1060℃において2時間焼成し、圧電セラミックスのサンプルを得た。その後、この円柱からスライス加工、ラップ加工を経て厚さ0.6mmのディスク状サンプルを得た。このディスクの両主面にAgをペースト印刷し、650℃で10分間の焼き付けを行った。その後、このディスクに対し、120℃のシリコンオイル中で3kV/mmの電界を印加して20分間の分極処理を行い、測定用サンプルとした。各測定用サンプルを24時間放置した後、インピーダンスアナライザー(HP4194A:YHP社製)を用いて径方向振動の電気機械結合係数(k_r)および比誘電率(ε_d)(1kHz)を測定した。k_rおよびε_dはEMAS-6100に従って求めた。また、強度試験を行うために、電極付けをしていないディスクを縦2.0mm×横4.0mm×厚さ0.6mmの寸法に切り出した。そのサンプルの抗折強度を、3点曲げ測定法を用いて、デジタル荷重試験機によりJIS(R1601)に準じて測定した。測定条件は、支店間距離:2.0mm、荷重速度:0.5mm/分であった。ここで作製したサンプルの組成は以下の通りであった。

(Pb_xSr_{0.99-x})[Ti_{0.45}Zr_{0.55}(Co_{1/3}Nb_{2/3})_{0.10}]O₃+0.6重量%WO₃; x=0.931, 0.935, 0.940, 0.945, 0.950, 0.955および0.959

尚、比較のために、x=0.930(A/B=0.970)、0.960(A/B=1.000)、0.970(A/B=1.010)のものも各々作製した。測定結果を併せて表1に示す。

【0017】

【実施例2】出発材料としてPbO、TiO₂、ZrO₂、ZnO、Nb₂O₅、添加物としてTa₂O₅を用い、分極処理を3kV/mmで20分間ではなく15分間行い、またk_rの代わりにk₃₃を測定した以外は実施例1と同様にしてサンプルを作製した。焼成温度も実施例1と同様に1060℃とした。ここで作製したサン

*ブルの組成は以下の通りである。

(Pb_x)[Ti_{0.45}Zr_{0.55}(Zn_{1/3}Nb_{2/3})_{0.10}]O₃+0.4重量%Ta₂O₅; x=0.971, 0.975, 0.980, 0.985, 0.990, 0.995および0.999

なお、比較のために、x=0.960(A/B=0.966)、0.970(A/B=0.970)、1.000(A/B=1.000)のものも各々作製した。測定結果を併せて表2に示す。

10 【0018】

【実施例3】出発材料としてPbO、TiO₂、ZrO₂、MgO、Nb₂O₅、SrCO₃、添加物としてNb₂O₅を用い、焼成温度を表3に示すように最大k_rが得られる温度とした以外は実施例2と同様にしてサンプルを作製した。ここで作製したサンプルの組成は以下の通りである。

(Pb_xSr_{0.99-x})[Ti_{0.45}Zr_{0.55}(Mg_{1/3}Nb_{2/3})_{0.25}]O₃+0.2重量%Nb₂O₅; x=0.931, 0.935, 0.940, 0.945, 0.950, 0.955および0.959

尚、比較のために、x=0.920(A/B=0.960)、0.930(A/B=0.970)、0.960(A/B=1.000)のもの、x=0.970(A/B=1.010)のものも各々作製した。測定結果を併せて表3に示す。

【0019】

【実施例4】出発材料としてPbO、TiO₂、ZrO₂、SnO₂、Sb₂O₃、SrCO₃、添加物としてSiO₂を用い、焼成温度を1200℃とした以外は実施例2と同様にしてサンプルを作製した。ここで作製したサンプルの組成は以下の通りである。

(Pb_xSr_{0.99-x})[Ti_{0.45}Zr_{0.55}(Sn_{1/2}Sb_{1/2})_{0.05}]O₃+0.08重量%SiO₂; x=0.935, 0.940, 0.945, 0.950, 0.955および0.959

尚、比較のために、x=0.960(A/B=1.000)、x=0.970(A/B=1.010)のものも各々作製した。測定結果を併せて表4に示す。

【0020】

【実施例5】添加物としてTa₂O₅に代えてNiO、PdCl₂、La₂O₃、Pr₆O₁₁、Nd₂O₃、Gd₂O₃をそれぞれ用い、またk₃₃の代わりにk_rを測定した以外は実施例2と同様にしてサンプルを作製した。測定結果を併せて表5に示す。

【表1】

Pb:xモル	A/B	強度(MPa)	ε _d	k _r (%)
0.930	0.970	116	1570	54.6
0.931	0.971	121	1620	55.2
0.935	0.975	125	1680	56.0
0.940	0.980	123	1730	57

7				8
0.945	0.985	123	1790	58.0
0.950	0.990	122	1850	59.3
0.955	0.995	118	1950	61.1
0.959	0.999	109	2010	64.1
0.960	1.000	112	2020	62.8
0.970	1.010	104	2020	65.5

【表2】

Pb : xモル	A/B	強度 (MPa)	ϵd	k33 (%)
0.960	0.960	121	1710	67.2
0.970	0.970	119	1860	69.3
0.971	0.971	119	1860	69.5
0.975	0.975	117	1910	70.5
0.980	0.980	114	1980	71.5
0.985	0.985	112	2020	73.0
0.990	0.990	109	2040	74.2
0.995	0.995	104	2050	74.4
0.999	0.999	95	1950	74.5
1.000	1.000	88	1790	74.5

【表3】

Pb : xモル	A/B	強度 (MPa)	ϵd	k _r (%)	焼成温度(°C)
0.920	0.960	111	2860	60	1200
0.930	0.970	106	3060	60.9	1200
0.931	0.971	109	3080	61.8	1200
0.935	0.975	108	3190	63.5	1170
0.940	0.980	108	3300	64.3	1170
0.945	0.985	107	3350	64.2	1170
0.950	0.990	104	3160	63.6	1150
0.955	0.995	102	3100	64.3	1150
0.959	0.999	92	3100	64.5	1060
0.960	1.000	92	3000	61.1	1200
0.970	1.010	81	2680	61	1060

【表4】

Pb : xモル	A/B	強度 (MPa)	ϵd	k _r (%)
0.935	0.975	120.2	2280	55.4
0.940	0.980	116.6	2360	56.9
0.945	0.985	110.3	2430	58.3
0.950	0.990	103.4	2500	59.9
0.955	0.995	105.8	2490	60.2
0.959	0.999	107.5	2490	60.5
0.960	1.000	107.1	2480	60.9
0.970	1.010	93.0	2400	59.3

【表5】

添加物	A/B	強度 (MPa)	ϵd	k _r (%)
NiO	0.99	102	1852	65.2
PdCl ₂	0.99	106	2360	65.9
La ₂ O ₃	0.99	101	2107	67.1
Pr ₆ O ₁₁	0.99	100	2424	65.8
Nd ₂ O ₃	0.99	103	2490	65.4
Gd ₂ O ₃	0.99	101	2422	65.7

【0021】表1～表5に示した測定結果から、本発明に係る圧電セラミック組成物は、優れた比誘電率、電気機械結合係数、圧電特性と、十分な機械的強度とを併せ持つものであることが分かる。

【0022】なお、本発明に係る圧電セラミック組成物においては、巨視的に見ると、 $a1 + a2 (A/B)$ の値が小さくなるにつれて、得られる製品組成物の機械的強度が増大し、一方比誘電率が減少する傾向があるため、かかる傾向を利用して、製品用途に適切に応じた所望の機械的強度および所望の比誘電率の双方を共に与え*

る組成を容易に決定し、その組成に係る製品組成物を得ることもできる。

【0023】

【発明の効果】本発明に係る圧電セラミック組成物によれば、超小型、薄型のアクチュエータ等の素子に加工した場合にも良好な比誘電率、電気機械結合係数、圧電特性を維持しながら、十分な機械的強度、特に抗折強度を有するセラミックスを提供することができ、その産業上の利用価値は極めて大きい。

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JAPANESE

[JP,2001-181033,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL
PROBLEM MEANS EXAMPLE

[Translation done.]

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 CLAIMS

[Claim(s)]

[Claim 1] Basic empirical formula: $[Pba_1Aa_2]$ and $[(B_1 B_2) x Ti y Zr z] O_3$ (among a formula) A is a kind of element chosen from calcium, Sr, Ba, and La at least.; B₁ Sn, They are Zn, Cd, Mg, nickel, Co, Fe, Sc, Yb, Lu, In, or Mn.; B₂ Sb, They are Nb, Ta, W, or Te.;, and a₁, a₂, x, y and z, respectively Conditional

expression : $x+y+z=10.05 \leq x \leq 0.400.1 \leq y \leq 0.50.2 \leq z \leq 0.60.97 < (a_1+a_2) < 1$ It is the atomic ratio which fills 1. As opposed to the oxide constituent expressed however -- although a₁ is not 0 -- a₂ -- 0 -- it can be -- Pd, B₂s aluminum [O₃ MgO, and] 2O₃, SiO₂ and Sc 2O₃, V₂O₅, Cr₂O₃, Mn₃O₄, Fe₂O₃, CoO, NiO, CuO, ZnO, GeO₂, Y₂O₃, Nb₂O₅, MoO₃, SnO₂ and Sb 2O₃, HfO₂ and Ta 2O₅, WO₃ and Bi 2O₃, La₂O₃, CeO₂ and Pr 6O₁₁, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, TbO, The piezo-electric ceramic constituent characterized by coming to add at least a kind of metal chosen from Dy 2O₃, Ho₂O₃, Er₂O₃, Yb₂O₃, and the group that consists of LuO, or an oxide 0.01 % of the weight to 1% of the weight.

[Claim 2] The piezo-electric ceramic constituent according to claim 1 which comes to add the matter which replaces with said oxide and can grow into said oxide by baking.

[Claim 3] The piezo-electric ceramic constituent according to claim 1 or 2 whose diameter of crystal grain is 5 micrometers or less in 0.1 micrometers or more.

 [Translation done.]

JAPANESE

[JP,2001-181033,A]

<u>CLAIMS</u>	<u>DETAILED DESCRIPTION</u>	<u>TECHNICAL FIELD</u>	<u>PRIOR ART</u>	<u>EFFECT OF THE INVENTION</u>	<u>TECHNICAL</u>
<u>PROBLEM</u>	<u>MEANS</u>	<u>EXAMPLE</u>			

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the piezo-electric ceramic constituent which comes as an additive to add a specific metal or a specific oxide to a piezo-electric ceramic constituent, especially the oxide constituent expressed with basic empirical formula $[Pb_{1-A}A_2] [(B_1 B_2) x Ti_y Zr_z] O_3$.

[0002]

[Description of the Prior Art] Conventionally, there is a piezo-electric ceramic constituent which consists of $[Pb_{1-A}SrbB_{1-A}C] A$ and $[(Zn_{1/3}Nb_{2/3}) Z Ti_x Zr_y] BO_3$ as a thing about amelioration of a ternary system piezo-electricity ceramic constituent (JP,3-256379,A), and the piezo-electric ceramic constituent which gave the big piezoelectric constant suitable for the activity as a sound transducer by setting the value of A/B as the specific range is indicated. Moreover, in the oxide constituent expressed with $xTi_yZr_zO (Mg(Pb_{1-a}bMa)_{1/3}Nb_{2/3})_3$, it is known for things for being referred to as $b=0.005-0.05$ that an electromechanical coupling coefficient and a dielectric constant can be made high (JP,4-78582,B).

[0003]

[Problem(s) to be Solved by the Invention] The piezo-electric ceramic ingredient is broadly used for various applications, such as a piezo-electric filter, a piezoelectric transformer, an ultrasonic vibrator, an electrostrictive actuator, and a piezo-electric buzzer. Especially, as for piezoelectric transducers, such as the piezo-electric sounding body and an electrostrictive actuator, a miniaturization and lamination are progressing in recent years. Especially, in the field of electronic parts, such as an electrostrictive actuator, development of the micro electrostrictive actuator which can offer very small displacement of submicron order is briskly performed with improvement in recording density, for example as a micro-actuator for the hard disk drive head for personal computers etc.

[0004] When using piezoelectric material as for example, an actuator for displacement control, in order to raise the displacement engine performance, it is necessary to enlarge a piezoelectric constant (d). Generally in piezoelectric material, there is relation it is unrelated $d^2/k\epsilon$ between a piezoelectric constant (d), and an electromechanical coupling coefficient (k) and specific inductive capacity (epsilon), and in order to enlarge a piezoelectric constant (d), an electromechanical coupling coefficient (k) and specific inductive capacity (epsilon) must be enlarged. The piezo-electric ceramic constituent which has the outstanding piezo-electric property conventionally from this viewpoint has been developed variously.

[0005] However, although the piezo-electric ceramic ingredient of the conventional presentation had the outstanding piezo-electric property, it had the trouble that a mechanical strength was not necessarily enough. That is, when these ingredients were used for the above-mentioned actuator etc., there was a fault that defects, such as a crack and a chip, arise in case it is processed into a component, or a crack arose with the stress from outside for the character near the structural material. Moreover, in order to obtain the big amount of displacement, when a big electrical potential difference was impressed on the occasion of actuation of a component, since the mechanical strength was insufficient, there was also a fault that it may result in destruction with the displacement itself.

[0006] Therefore, having the outstanding specific inductive capacity, an electromechanical coupling coefficient, and a piezo-electric property, this invention aims at offering the piezo-electric ceramic constituent which has sufficient mechanical strength, also when it is processed into micro and a thin component.

[0007]

[Means for Solving the Problem] In the oxide constituent by which the constituent concerning this invention is expressed

with basic empirical formula $[Pb_{1-2}A_{2-2}][(B_1-B_2) \times Ti_y Zr_z] O_3$ The value of a_1+a_2 , Namely, when the ratio (henceforth A/B) to the presentation ratio of the $[(B_1-B_2) TiZr]$ site of the presentation ratio of the $[PbA]$ site is made smaller than 1 and specification [a specific metal or a specific oxide] carries out amount addition as an additive It is based on discovery that a mechanical strength, especially anti-chip box reinforcement improve, maintaining good specific inductive capacity, an electromechanical coupling coefficient, and a piezo-electric property.

[0008] This invention based on this discovery is basic empirical formula: $[Pb_{1-2}A_{2-2}][(B_1-B_2) \times Ti_y Zr_z] O_3$ (among a formula). A is a kind of element chosen from calcium, Sr, Ba, and La at least.; B1 Sn, They are Zn, Cd, Mg, nickel, Co, Fe, Sc, Yb, Lu, In, or Mn.; B-2 Sb, They are Nb, Ta, W, or Te.;, and a_1 , a_2 , x , y and z , respectively Conditional expression : $x+y+z=10.05 \leq x \leq 0.400.1 \leq y \leq 0.50.2 \leq z \leq 0.60.97 < (a_1+a_2) < 1$ It is the atomic ratio which fills 1. As opposed to the oxide constituent expressed however -- although a_1 is not 0 -- a_2 -- 0 -- it can be -- Pd, B-2s aluminum [O_3 MgO, and] $2O_3$, SiO_2 and Sc_2O_3 , V_2O_5 , Cr_2O_3 , Mn_3O_4 , Fe_2O_3 , CoO , NiO , CuO , ZnO , GeO_2 , Y_2O_3 , Nb_2O_5 , MoO_3 , SnO_2 and Sb_2O_3 , HfO_2 and Ta_2O_5 , WO_3 , Bi_2O_3 , La_2O_3 , CeO_2 and Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , TbO_3 , It is the piezo-electric ceramic constituent characterized by coming to add at least a kind of metal chosen from Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Yb_2O_3 , and the group that consists of LuO , or an oxide 0.01 % of the weight to 1% of the weight. In this invention, as mentioned above, the value of a_1+a_2 , i.e., A/B, is larger than 0.97, and a small thing is more desirable than 1. If the value of A/B becomes 0.97 or less, as for required high specific inductive capacity and electromechanical coupling coefficient *****, a piezo-electric property will no longer be easy to be acquired. When it measures by the required high mechanical strength, for example, the measuring method mentioned later, it becomes impossible moreover, to obtain the mechanical strength of 100 or more MPas, if the value of A/B becomes one or more.

[0009]

[Embodiment of the Invention] Next, the desirable operation gestalt of the piezo-electric ceramic constituent of this invention is explained. First, using the compound which can replace an oxide by baking like an oxide or a carbonate, a nitrate, or a hydroxide as a start ingredient, weighing capacity of them is carried out so that it may become the quantitative ratio which gives the predetermined last presentation, and they carry out wet blending using a ball mill etc. As a slurry medium in the case of this wet blending, it is desirable to use the mixture of alcohol, such as water or ethanol, or water and alcohol.

[0010] In this invention, said start raw material is preferably received after this temporary baking later mentioned at the mixing time. Pd, B-2s aluminum [O_3 MgO, and] $2O_3$, SiO_2 and Sc_2O_3 , V_2O_5 , Cr_2O_3 , Mn_3O_4 , Fe_2O_3 , CoO , NiO , CuO , ZnO , GeO_2 , Y_2O_3 , Nb_2O_5 , MoO_3 , SnO_2 and Sb_2O_3 , HfO_2 and Ta_2O_5 , WO_3 and Bi_2O_3 , La_2O_3 , CeO_2 and Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , TbO_3 , Dy_2O_3 -- O_3 and Ho_2O_3 -- O_3 and Er_2O_3 -- O_3 and Yb_2O_3 -- at least a kind of metal or oxide chosen from the group which consists of O_3 and LuO -- criteria [weight / of a start raw material / sum total] -- carrying out -- 0.01 % of the weight - 1 % of the weight -- amount addition is carried out. When using combining the plurality of this oxide, it is desirable that the addition of two or more sum totals is 0.01 % of the weight - 1 % of the weight. In addition, when not filling an addition to 0.01% of the weight, the effectiveness of an additive is not accepted, but if an addition exceeds 1 % of the weight, on the other hand, adverse effects, such as lowering of a dielectric constant and an electromechanical coupling coefficient, will become remarkable on the contrary.

[0011] In addition, in this invention, it may replace with the above-mentioned oxide and the matter which can grow into the above-mentioned oxide by baking, for example, a carbonate, a nitrate, a hydroxide, or a metal may be added. When replacing with the above-mentioned oxide and adding this matter, as for the addition, it is desirable to convert into the weight of a corresponding oxide and to consider as 0.01 % of the weight - 1 % of the weight (sum total weight criteria of a start raw material). When using combining the plurality of this matter, it is desirable like the above that the total quantity when converting into the weight of each corresponding oxide is 0.01 % of the weight - 1 % of the weight.

[0012] After fully mixing a start raw material, temporary baking is carried out in the temperature of about 800 - 1000 degrees C of abbreviation for abbreviation 1- about 3 hours, the obtained temporary pottery is slurred and wet grinding is carried out using a ball mill etc. As a slurry medium in the case of this wet grinding, it is desirable to use the mixture of alcohol, such as water or ethanol, or water and alcohol. In addition, as for this wet grinding, it is desirable to carry out until the mean particle diameter of the grinding particle of temporary pottery is set to about 0.5-2.0 micrometers.

[0013] The powder of the obtained temporary pottery is dried after wet grinding, small quantity (0.5 % of the weight - 8 % of the weight) addition of the binders, such as water or polyvinyl alcohol, is carried out, press forming is carried out to a dry matter by the pressure of 98-392MPa (1 - 4 tf/cm²), and a Plastic solid is acquired. In addition, as a fabricating method, the extrusion casting method and other casting methods usually used by this technical field can also be used.

[0014] Subsequently, a Plastic solid is calcinated and electrostrictive ceramics is obtained. Burning temperature chooses the temperature within the limits of 1060 degrees C - 1200 degrees C preferably. Moreover, firing time is preferably made into about 1 - 4 hours. Baking may be performed in atmospheric air and you may carry out in the ambient atmosphere where oxygen tension is higher than the inside of atmospheric air, and a pure oxygen ambient atmosphere.

[0015] In this invention, in the case of baking, it is desirable to make it the diameter of crystal grain of the ceramics obtained set to 0.1 micrometers or more and 5 micrometers or less, and if grain growth is carried out more greatly than 5 micrometers, the inclination for a mechanical strength to fall will be seen.

[0016]

[Example]

[Example 1] After carrying out weighing capacity and blending as a start raw material so that it may become the quantitative ratio which gives the predetermined last presentation for them, using WO_3 as PbO , TiO_2 , ZrO_2 , CoO , Nb_2O_5 , SrCO_3 , and an additive, wet blending was carried out for 5 hours using the ball mill. As a slurry medium, water was used at the time of wet blending. Subsequently, temporary baking of the mixture was carried out in 900 degrees C for 2 hours, and wet grinding was carried out for 15 hours using the ball mill after that. As a slurry medium, water was used at the time of wet grinding. Water was added 6% of the weight to the powder-like dry matter after drying a slurry, 1 shaft pressing was carried out under the pressure of 39.2MPa (400 kgf/cm²), the cylinder was produced, and cold isostatic pressing of 392MPa(s) (4 t/cm²) was performed to this. This cylinder was calcinated in 1060 degrees C for 2 hours, and the sample of electrostrictive ceramics was obtained. Then, the disk-like sample with a thickness of 0.6mm was obtained from this cylinder through slice processing and lap processing. Paste printing of Ag was carried out and baking for 10 minutes was performed to both the principal planes of this disk at 650 degrees C. Then, to this disk, 3kV [mm] electric field were impressed in 120-degree C silicone oil, polarization processing for 20 minutes was performed, and it considered as the sample for measurement. After leaving each sample for measurement for 24 hours, the electromechanical coupling coefficient (kr) and specific inductive capacity (epsilond) of the direction oscillation of a path (1kHz) were measured using the impedance analyzer (H.P. product made from 4194 A:YHP). It asked for kr and epsilond according to EMAS-6100. Moreover, in order to perform a strength test, the disk which has not carried out electrode attachment was cut down in the dimension with a 4.0mm[2.0mm by] x thickness of 0.6mm. The anti-chip box reinforcement of the sample was measured according to JIS (R1601) using the three-point bending measuring method with the digital load test machine. The Measuring condition was a part for distance:2.0mm, and loading-rate:0.5mm/between branch offices. The presentation of the sample produced here was as follows.

($\text{Pb}_x\text{Sr}_{0.040}$) The thing of $x = 0.930$ ($A/B=0.970$), and 0.960 ($A/B=1.000$) and 0.970 ($A/B=1.010$) was also respectively produced for [$\text{Ti}_{0.458}\text{Zr}_{0.532}$ ($\text{Co}_{1/3}\text{Nb}_{2/3}$) 0.010] $\text{O}_3+0.6\%$ of the weight WO_3 ; $x=0.931, 0.935, 0.940, 0.945, 0.950, 0.955$ and 0.959, in addition a comparison. A measurement result is combined and is shown in a table 1.

[0017]

[Example 2] The sample was produced for polarization processing as a start ingredient like [3kV/mm] the example 1 but [not for 20 minutes] except having carried out for 15 minutes and having measured k33 instead of kr, using Ta_2O_5 as PbO , TiO_2 , ZrO_2 , ZnO , Nb_2O_5 , and an additive. Burning temperature as well as an example 1 was made into 1060 degrees C. The presentation of the sample produced here is as follows.

(Pb_x) [$\text{Ti}_{0.420}\text{Zr}_{0.480}$ ($\text{Zn}_{1/3}\text{Nb}_{2/3}$) 0.100] $\text{O}_3+0.4\%$ of the weight Ta_2O_5 ; $x=0.971$, and 0.975, 0.980, 0.985, 0.990, 0.995 and 0.999 -- in addition, the thing of $x = 0.960$ ($A/B=0.96$), and 0.970 ($A/B=0.970$) and 1.000 ($A/B=1.000$) was also respectively produced for the comparison. A measurement result is combined and is shown in a table 2.

[0018]

[Example 3] as a start ingredient -- PbO , TiO_2 , ZrO_2 , MgO , and Nb_2O_5 -- burning temperature is shown in a table 3, using Nb_2O_5 as O_5 , SrCO_3 , and an additive -- as -- a maximum of -- the sample was produced like the example 2 except having considered as the temperature from which kr is obtained. The presentation of the sample produced here is as follows.

($\text{Pb}_x\text{Sr}_{0.040}$) [$\text{Ti}_{0.400}\text{Zr}_{0.335}$ ($\text{Mg}_{1/3}\text{Nb}_{2/3}$) 0.265] $\text{O}_3+0.2\%$ of the weight Nb_2O_5 ; $x=0.931$, and 0.935, 0.940, 0.945, 0.950, 0.955 and 0.959 -- in addition, the thing of $x = 0.920$ ($A/B=0.960$), and 0.930 ($A/B=0.970$) and 0.960 ($A/B=1.000$) and the thing of $x = 0.970$ ($A/B=1.010$) were also respectively produced for the comparison. A measurement result is combined and is shown in a table 3.

[0019]

[Example 4] The sample was produced like the example 2 as a start ingredient except having made burning temperature

into 1200 degrees C, using SiO₂ as PbO, TiO₂, ZrO₂, SnO₂, Sb₂O₃, SrCO₃, and an additive. The presentation of the sample produced here is as follows.

(Pb_xSr_{0.040}) The thing of $x = 0.960$ ($A/B = 1.000$) and $x = 0.970$ ($A/B = 1.010$) was also respectively produced for [Ti_{0.460}Zr_{0.460} (Sn_{1/2}Sb_{1/2} 0.080) O₃+0.08 % of the weight SiO₂: $x = 0.935, 0.940, 0.945, 0.950, 0.955$ and 0.959 , in addition a comparison. A measurement result is combined and is shown in a table 4.

[0020]

[Example 5] The sample was produced like the example 2 except having replaced with Ta₂O₅ as an additive, and having measured k_r instead of k_{33} , using respectively NiO, PdCl₂, La₂O₃, Pr₆O₁₁, Nd₂O₃, and Gd₂O₃. A measurement result is combined and is shown in a table 5.

[A table 1]

Pb: x mol A/B Reinforcement (MPa) ϵ_{kr} (%) 0.930 0.970 116 1570 54.60.931 0.971 121 1620 55.20.935 0.975 125 1680 56.00.940 0.980 123 1730 57.0.945 0.985 123 1790 58.00.950 0.990 1221850 59.30.955 0.995 118 1950 61.10.959 0.999 109 2010 64.10.960 1.000 1122020 62.80.970 1.010 104 2020 65.5 [A table 2]

Pb: x mol A/B Reinforcement (MPa) ϵ_{k33} (%) 0.960 0.960 121 1710 67.20.970 0.970 119 1860 69.30.971 0.971 119 1860 69.50.975 0.975 117 1910 70.50.980 0.980 114 1980 71.50.985 0.985 112 2020 73.00.990 0.990 109 2040 74.20.9950.995 104 2050 74.40.999 0.999 95 1950 74.51.000 1.000 88 1790 74.5 [a table 3]

Pb: x mol A/B Reinforcement (MPa) ϵ_{kr} (%) Burning temperature (degree C) 0.920 0.960 111 2860 60 12000. 930 0.970 106 3060 60.9 12000.931 0.971 109 3080 61.8 12000.935 0.975 108 3190 63.5 11700.940 0.980 108 3300 64.3 11700.945 0.985 107 3350 64.2 11700.950 0.990 104 3160 63.6 11500.955 0.995 102 3100 64.3 11500.959 0.999 92 3100 64.5 10600.960 1.000 92 3000 61.1 12000.970 1.010 81 2680 61 1060 [A table 4]

Pb: x mol A/B Reinforcement (MPa) ϵ_{kr} (%) 0.935 0.975 120.2 2280 55.40.940 0.980 116.6 2360 56.90.945 0.985 110.3 2430 58.30.950 0.990 103.4 2500 59.90.955 0.995 105.8 2490 60.20.959 0.999 107.5 2490 60.50.960 1.000 107.1 2480 60.90.970 1.010 93.0 2400 59.3 [A table 5]

Additive A/B Reinforcement (MPa) ϵ_{kr} 103 2490 65.4Gd₂O₃ 0.99 1012422 65.7 k_r (%) NiO 0.99 102 1852 65.2PdCl₂ 0.99 106 2360 65.9La₂O₃ 0.99 101 2107 67.1Pr₆O₁₁ 0.99 100 2424 65.8Nd₂O₃ 0.99 [0021] The

measurement result shown in a table 1 - a table 5 shows that the piezo-electric ceramic constituent concerning this invention is a thing having the outstanding specific inductive capacity, an electromechanical coupling coefficient, a piezo-electric property, and sufficient mechanical strength.

[0022] In addition, it sets to the piezo-electric ceramic constituent concerning this invention, The mechanical strength of the product constituent obtained as the value of $a_1 + a_2$ (A/B) will become small, if it sees macroscopically increases, since there is an inclination for specific inductive capacity to decrease on the other hand, using this inclination, the presentation which gives both the both sides of the mechanical strength of the request which responded suitable for a product application, and desired specific inductive capacity can be determined easily, and the product constituent concerning the presentation can also be obtained.

[0023]

[Effect of the Invention] According to the piezo-electric ceramic constituent concerning this invention, maintaining good specific inductive capacity, an electromechanical coupling coefficient, and a piezo-electric property, also when it is processed into components, such as micro and a thin actuator, the ceramics which has sufficient mechanical strength, especially anti-chip box reinforcement can be offered, and the utility value on the industry is very large.

[Translation done.]